

Gas Standards Based on Optical Spectroscopies

New applications for gas standards demand high-precision measurements of low concentrations of reactive and non-reactive gases. This challenge requires developing a new generation standards linked to intrinsic molecular properties. We plan to realize and disseminate new primary gas standards using quantitative absorption spectroscopy. To this end, we are combining: (1) frequency-stabilized cavity ring-down spectroscopy (FS-CRDS), (2) low-uncertainty methods of sample preparation and, (3) absolute measurements of absorption line intensities for low-molecular-mass target analytes; e.g., small hydrocarbons, H₂O, NO, NO₂, O₃, and NH₃. The advantages of CRDS as a primary measurement technique include: compact sample volumes, low uncertainty, high spectral resolution, and high sensitivity.

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The goal of this program is to shift the principal realization of traceable gas measurement from consumable artifacts to intrinsic standards. For certain molecules, particularly reactive gases, recent and anticipated advances in spectroscopic measurements will make robust intensity measurements viable for quantitative gas metrology. We anticipate an accuracy rivaling and potentially surpassing traditional measurements using artifact standards.

During 2005 we used frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) to complete a comprehensive series of high-resolution line shape measurements. Oversimplified models of line shapes lead to systematic errors in the determination of line intensity and in analyte number density. In this study, we probed near-infrared transitions of water vapor and considered foreign-broadening by He, N₂, and SF₆ as well as self-broadened line shapes. A number of line shape models incorporating effects such as collisional narrowing, speed-dependent pressure shifting, and pressure broadening and correlations between velocity- and phase-changing collisions were evaluated.

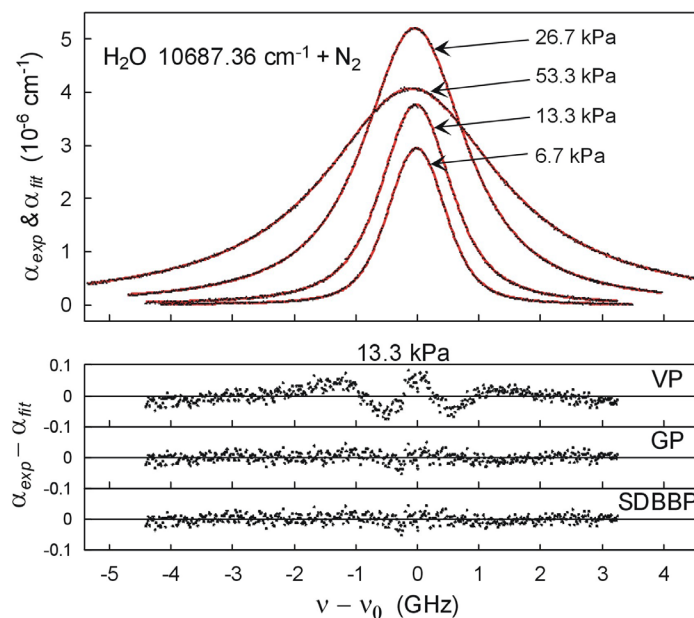
The figure to the right (top) shows a CRDS-measured H₂O spectrum (points) and fitted model (solid lines) for various pressures, p , of N₂. The bottom figure of the graphic shows fit residuals for a $p=13.3$ kPa profile corresponding to indicated line shape models.

We showed that differences in line intensities determined by fitting commonly used line shape models to the same high-resolution absorption spectra can be more than a few percent. Furthermore, we showed that line intensities with relative standard uncertainties less 0.3 % can be obtained by

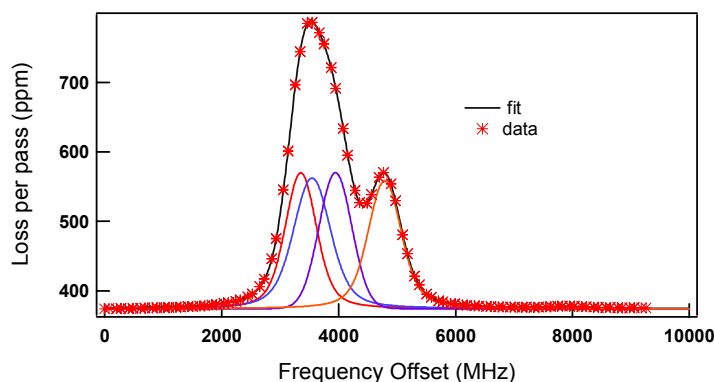
fitting physically appropriate models to the spectra. In other FS-CRDS experiments, we measured the line intensities of approximately 50 transitions in the 935 nm band of H₂O, and these intensities were linked to NIST primary thermodynamic humidity standards. The frequency stabilization inherent to the ring-down cavity experiment also enabled us to investigate difficult-to-observe saturation effects in CRDS spectra, which may bias spectroscopic measurements of number density.

The results of this research show that the spectral resolution of FS-CRDS is at least four orders of magnitude smaller than the Doppler widths of the absorption transitions investigated, thus illustrating the potential of FS-CRDS-based saturation spectroscopy for low-uncertainty measurements of absolute transition frequencies and pressure shifts.

Recent efforts have focused on testing the feasibility of delivering gas standards other than water vapor through intrinsic spectroscopic properties. To this end, we completed and tested an FS-CRDS system at 1.65 μm designed to probe $2\nu_3$ transitions CH₄. We have achieved a signal-to-noise of 40 for a 1 $\mu\text{mol. mol}^{-1}$ sample of CH₄ using ring-down cavity mirrors with a reflectivity $R=0.9997$. Based on these results, we project a detection limit of approximately 0.8 nmol. mol⁻¹, using mirrors with $R=0.9999$.



The figure below shows a spectrum for a 100 $\mu\text{mol. mol}^{-1}$ sample of CH_4 in air. We are currently comparing FS-CRDS measurements of 12 CH_4 -in-air SRMs to the assigned mole fraction values which range between 1 $\mu\text{mol. mol}^{-1}$ and 100 $\mu\text{mol. mol}^{-1}$.



CRDS-measured spectrum and multi-line fit to the data for $2\nu_3$ transitions of CH_4 at $1.65 \mu\text{m}$.

During 2005 we also began developing a portable FS-CRDS apparatus with broader application to other NIST projects involving trace water vapor for humidity standards and atomic-layer film deposition processes. This portable and automated system, which uses fiber-optic coupled distributed-feedback laser technology, will be readily adaptable to probe species such as NH_3 and CH_4 for gas standards applications.

Impact: The realization of intrinsic gas standards based on quantitative absorption spectroscopy will extend NIST capabilities in gas standards to lower concentrations, to reactive species that are unsuitable for long-term storage in cylinders, and to trace impurities in bulk process gases. Additional advantages to customers include: lower uncertainties, coverage of new species, potentially lower cost for standard mixtures, more flexibility in terms of dilution gas(es), and the availability of low-uncertainty molecular property data universally applicable to spectroscopic

measurements of gas concentration. Customers include current and new consumers of NIST standard gas mixtures, and users of molecular spectroscopy line intensity data. This work is relevant to emissions of toxic industrial compounds and emissions from ground and air transportation systems, air pollution monitoring (US Environmental Protection Agency), metrology of high-purity gases for semiconductor and photonics manufacturing, terrestrial and extraterrestrial atmospheric science (National Aeronautics and Space Administration), defense (Department of Defense and Department of Energy), health-care diagnostics and homeland security (Department of Homeland Security).

Future Plans: During 2006, we will use FS-CRDS to measure infrared spectral line shapes and line intensities of H_2O ($1.38 \mu\text{m}$ band) and CH_4 ($1.65 \mu\text{m}$ band), and we will apply CRDS to reactive species such as NH_3 . The portable CRDS spectrometer will be completed and applied to measurements of trace water vapor produced by NIST primary humidity standards. Finally, we will test an infrared absorption spectrometer for enabling real-time measurements of tropospheric O_3 , NO_2 , and NO .

References:

- J.T. Hodges and R. Ciurylo, "**Automated high-resolution frequency-stabilized cavity ring-down spectrometer**," Rev. Sci. Instrum., **76**, 023112 (2005).
- D. Lisak, J.T. Hodges and R. Ciurylo "**Comparison of semi-classical line shape models to rovibrational H_2O spectra measured by frequency-stabilized cavity ring-down spectroscopy**," Phys. Rev. A., **73**, 012507 (2006).
- D.D. Nelson, M.S. Zahniser, B. McManus, "**Quantum Cascade Laser Monitor for NO , NO_2 , and O_3** ", Aero-dyne Research Inc., Billerica, MA, 01821. Supported through NIST Small Business and Innovative Research Program (SBIR), Phase II completed Sept. 2005.